

COAL SOLUBILITY AND SWELLING

Paul Painter, Yung Park, John Graf,
Maria Sobkowiak and Mike Coleman
Polymer Science Program
The Pennsylvania State University
University Park, PA 16802

Key Words: Coal solubility, coal swelling, hydrogen bonding

INTRODUCTION

The characterization of coal as a macromolecular network has resulted in a significant advance in our understanding of this complex material. By applying the theories of Paul Flory (1,2), the solubility (or, more accurately, extractability) and swelling of a coal can be used as a probe of structure (3-11). It is widely recognized however, that the original theories are flawed, particularly the Flory-Rehner treatment of the swelling of polymer networks (although it apparently benefits from the cancellation of errors (12)), and their application to coals is further limited by the presumed non-Gaussian behaviour of the "chains" and the realization that coal segments interact with each other and solvent through the formation of hydrogen bonds. Strong, specific interactions such as these are not accounted for in Flory's original equations describing the free energy of mixing and the contribution of the chemical potentials to the balance of forces involved in the swelling of a cross-linked network. We have recently developed an association model that can account for hydrogen bonding in polymer mixtures (13-16). The result is a Flory-Huggins equation accounting for the entropy of mixing and the dispersive (and other) non-hydrogen bonding forces described by a χ parameter, with an addition free energy term ΔG_H that accounts for the change in the number and type of hydrogen bonds that occur as a function of composition;

$$\frac{\Delta G_M}{RT} = \frac{\phi_A}{x_A} \ln \phi_A + \frac{\phi_B}{x_B} \ln \phi_B + \phi_A \phi_B \chi + \frac{\Delta G_H}{RT} \quad (1)$$

where ϕ_A, ϕ_B are volume fractions and x_A, x_B are "degrees of polymerization", or, more accurately, the ratio's of the molar volumes of the components relative to a reference molar volume. The crucial points concerning this equation are:

- 1) The ΔG_H term is negative and favourable to mixing
- 2) The quantities used to calculate ΔG_H are determined experimentally and there are no adjustable parameters in this term
- 3) Phase behaviour is determined by the balance between the positive and unfavourable to mixing χ term and the favourable to mixing entropic and ΔG_H terms and the contribution of these terms to the derivatives of the free energy with respect to composition.

The equations for ΔG_H and its derivatives and the details of their specific application to coal have been presented elsewhere (17,18). Here we will concern ourselves with a brief outline of some of our most important recent results. Space does not permit a detailed description of the calculations, which will be presented in a set of three papers that are about to be submitted for publication (19-21). Our discussion will touch upon;

- a) The determination of χ from solubility parameters.
- b) The calculation of "hypothetical" phase diagrams for coal solutions
- c) The calculation of the molecular weight between cross-link points from swelling measurements
- d) The formulation of a new model for the description of coal swelling and its relationship to structure.

COAL SOLUBILITY PARAMETERS

If we are limiting its application to non-specific and (relatively) weak interactions, then the value of the Flory χ parameter can be estimated from solubility parameters using

$$\chi = \frac{V_B}{RT} (\delta_c - \delta_s)^2 + 0.34 \quad (2)$$

where V_B is a reference volume and δ_c and δ_s are the solubility parameters of the coal and solvent, respectively. For an insoluble network the solubility parameter (δ_c) has been determined in one of two ways: from group contributions using, for example, the methods of van Krevelen (4,22) Hoy (23) or Small (24), or from swelling measurements. Unfortunately, both these methods involve difficulties and for coals lead to the prediction of very different solubility parameters, even when the effect of hydrogen bonding is minimized or excluded. For example, Larsen et al. (7) carefully examined the swelling of acetylated coals in non-hydrogen bonding solvents. An Illinois No. 6 and a Bruceton coal both gave a maximum degree of swelling for solvents with solubility parameters in the range 9-10 (cal/cm³)^{1/2}. This value would then normally be taken as the proper value for coal, as it would give the minimum value for χ . However, a calculation of the corresponding solubility parameters using the atomic contribution method proposed by van Krevelen (4) gives values in the range 11-12 (cal/cm³)^{1/2}, depending upon the precise value of the fraction aromaticity assumed for these samples. We found it difficult to understand precisely how van Krevelen obtained his parameters, as his methodology is not described, but on the basis of our calculations we believe it to be prone to large errors and fully of broad and perhaps unjustifiable assumptions, as we will discuss in detail elsewhere in a separate publication (19). The obvious choice would therefore seem to be the experimentally determined values. Paradoxically, we believe that van Krevelen's result is at least in the right range and the value obtained from maximum swelling is not the value for coal. This is not because of any problem with the experiments, but one that has its origins in free volume or compressibility effects that are ignored in simple theories of mixing.

In resolving the differences in the values of δ_c given by group contributions and swelling measurements we first observe that this problem is not unique to coal. Bristow and Watson (26) found that certain rubbers with solubility parameter values of the order of 9-10, gave maximum swelling in a series of n-alkanes with heptane, $\delta=7.4$. This difference was demonstrated to be due to so-called free volume effects by Biros et al. (27), who applied Flory's equation-of-state theory (2). It is a relatively straightforward matter to show that such effects also account for the observed maximum in the swelling of coal. We have applied the lattice fluid model of Sanchez and Lacombe (28-30) rather than Flory's theory, however.

The association formalism we use to describe hydrogen bond interactions and the Sanchez-Lacombe theory are both simple lattice models, so for future application it is more appropriate to combine these approaches, as we will report elsewhere (31), than to somehow graft an association model onto Flory's equation-of-state. Accordingly, using the equations of Sanchez and Lacombe (28-29) the Flory χ parameter can be written as:

$$\chi = \frac{\bar{p}\Delta\epsilon^*}{RT} + \frac{1}{\phi_2} \left[\bar{T}_1 (\bar{p}_1 - \bar{p}) + \frac{(1-\bar{p})}{\bar{p}} \ln (1-\bar{p}) - \frac{(1-\bar{q})}{\bar{q}} \ln (1-\bar{q}) + \frac{1}{\bar{r}} \ln (\bar{p}/\bar{p}_1) \right] \quad (3)$$

or, more simply

$$\chi = \frac{\bar{p}\Delta\epsilon^*}{kT} + \beta^1 \quad (4)$$

where \bar{p} , T are the reduced density and temperature (see references 27-29) and the subscripts 1 and 2 refer to components 1 and 2 of the mixture. The term $\Delta\epsilon^*$ is given by

$$\Delta\epsilon^* = \epsilon_{11}^* + \epsilon_{22}^* - 2\epsilon_{12}^* \quad (5)$$

and is the usual difference in the energy of 1-2 contacts relative to 1-1,2-2 contacts. If we make the geometric mean assumption

$$\epsilon_{12}^* = (\epsilon_{11}^* \epsilon_{22}^*)^{1/2} \quad (6)$$

then

$$\chi = \frac{\bar{p}}{kT} \left[(\epsilon_{11}^*)^{1/2} - (\epsilon_{22}^*)^{1/2} \right]^2 + \beta^1 \quad (7)$$

The correspondence of this equation to the solubility parameter approach can then be seen immediately by rewriting equation 1 on the basis of numbers of molecules rather than moles and transforming the subscripts:

$$\chi = \frac{V_1}{kT} (\delta_1 - \delta_2)^2 + \beta \quad (8)$$

The solubility parameters are related to the cohesive energy densities (CED) and hence the lattice fluid parameters (28,29) through

$$\delta = (\text{CED})^{1/2} = \left(\frac{\Delta E_v}{V} \right)^{1/2} = \left(\frac{\epsilon^*}{v^*} \right)^{1/2} \bar{p} \quad (9)$$

where v^* is the average close packed volume of a segment and generally varies with composition (i.e., $v_1^* \neq v_2^*$). If we assume there is no dependence of the energies of interaction (ϵ_{11}^* etc.) on composition and use the identity $V_1 = v_1^*/\bar{p}_1$, then equation (8) can be obtained directly from equation 7. Accordingly, in the solubility parameter approach we can identify the parameter β with so-called free volume or compressibility effects, while the $(\delta_1 - \delta_2)^2$ term reflects exchange interaction energies that are assumed independent of composition. We must now face the following question: for coal is the value of β of the order of 0.34, as in many polymer systems, or are free volume differences such that there is a larger deviation? It is a relatively straightforward matter to use equation 3 to calculate χ for various coal/solvent mixtures. The necessary parameters for the solvents used by Larsen et al. (7) were obtained from Sanchez and Lacombe (28), while the parameters for coal were calculated from its coefficient of thermal expansion ($\alpha = 1 \times 10^{-5}$, from van Krevelen (34) and an assumed value of the solubility parameter of $\delta_c = 11.8$, a value estimated from van Krevelen's method (4). Coal-solvent interactions were also assumed to be given by the usual geometric mean assumption. The equations necessary for these calculations are given elsewhere (19) and here we simply present the result in Figure 1, a plot of χ vs δ_s . A coal with a solubility parameter of $11.8 (\text{cal/cm}^3)^{1/2}$ has a minimum value of χ and hence a predicted maximum swelling with a solvent that has a solubility parameter of

about $10 \text{ (cal/cm}^3)^{1/2}$. A value of δ for an Illinois #6 coal of 11.4, as we estimate from a revised methodology (19) gives a predicted maximum swelling with non-hydrogen bonding solvents that have a solubility parameter in the range 9-10, corresponding to the value determined experimentally by Larsen et al. (7).

THE PHASE BEHAVIOUR OF SOLUTIONS OF COAL MOLECULES

An understanding of the solubility of a coal in various solvents can be obtained by a calculation of hypothetical phase diagrams. They are hypothetical in the sense that we assume that the coal is not cross-linked, but is simply a macromolecule. This macromolecule could be highly branched and with an extremely high molecular weight, but within the limitations of the simple lattice model applied here its equilibrium properties can be determined. This, in turn, allows an understanding of why a particular solvent is capable of extracting more (or less) soluble material than another and, as we will see, provides some fundamental insight into the variation of swelling behavior with temperature.

In a preliminary communication of this work (18) we calculated theoretical phase diagrams as a function of coal rank. the value of χ was estimated using van Krevelens method (4). As we will discuss in detail in a separate paper (19), we have little confidence in the precise value so calculated for any particular coal, but the trend with rank makes sense in terms of what we know about the structure of coal and the value appears to be in the right range. The calculation of the ΔG_H term and the derivatives of the free energy are described in previous publications (13-18). here we will discuss the calculated spinodals for three coals, an Illinois #6, PSOC 207 and PSOC 402, shown in Figures 2-4, as these results bear on the interpretation of swelling measurements.

For Illinois #6 coal we illustrate the spinodals obtained for mixing with three different solvents, pyridine, THF and benzene. For pyridine, we predict a typical inverted "U" shaped stability curve with an upper critical solution temperature near 25°C . Mixtures with THF and benzene are predicted to be far less miscible, with the stability limits calculated to be near the two composition extremes. An examination of Table 1, which lists the solvent parameters utilized here, together with some values for other solvents, immediately demonstrates why. Pyridine forms much stronger hydrogen bonds than the other solvents listed (as measured by the equilibrium constant K_A) and, in addition, its solubility parameter is closer to the range we estimate represents the most likely value for this coal ($11-12 \text{ (cal/cm}^3)^{1/2}$). Thus, favorable interactions (coal solvent hydrogen bonds) are maximized and χ is minimized. This is a crucial point, correlation of coal swelling to a single parameter, chosen so as to represent χ or some measure of the strength of favorable interactions, can be misleading. It is the balance of favorable and unfavorable forces that is crucial.

The calculated spinodals for PSOC 207 and PSOC 402 in pyridine show progressively increasing values of the upper critical solution temperature (maximum value of the inverted "U") relative to Illinois #6 coal, a trend that largely reflects the increasing value of χ calculated for this coal-pyridine series. To reiterate, although the precise positions of these curves are obviously affected by the errors in calculating δ_c , we believe that this predicted trend in behavior should be reasonably accurate.

The calculated phase behaviours indicates that if these coals were not cross-linked they would be completely soluble in pyridine at elevated temperatures. This remains true even if we assume very high molecular weights for the coal molecules (the contribution of the combinatorial entropy from the coal is very small for the degree of polymerization x_B assumed in these calculations ($x_B=100$); changing this value to 1000 or 10,000 has only a minor effect on the calculated spinodals, as illustrated in our preceding publications (17,18)). Accordingly, we believe that these results strongly support the present generally held view that at least up to a certain carbon content, coals are cross-linked networks

THE SWELLING OF COAL

Hydrogen bonding affects the swelling of coal through its contribution to the chemical potential of the solvent (ΔG_H). The Flory Rehner equation, as modified by Kovac (32) and applied to coal by Larsen et al. (7), can then be written

$$\bar{M}_c = \frac{\rho_B V_A \phi_B^{1/3} + \rho_B V_A / N \phi_B^{1/3}}{\left[\ln(1 - \phi_B) + \phi_B + \chi \phi_B^2 + \left(\frac{\Delta G_H}{RT} \right)_A \right]} \quad (10)$$

where \bar{M}_c is the number average molecular weight between cross link points and N represents the number of "clusters" between cross link points. Larsen et al. (7) studied the swelling of an extracted but otherwise unreacted Illinois #6 coal in pyridine. Using the reported swelling ration of about $Q=2.4$, we obtained the plots of \bar{M}_c , the number average molecular weight between cross link points against M_0 , the assumed molecular weight of a coal cluster, shown in Figure 5. In this initial plot we put $(\Delta G_H)_A = 0$, i.e., we ignored hydrogen bonding. Results were obtained for four different assumed values of δ_{coal} , ranging from 9 to 12 and display the large sensitivity to χ noted by Lucht and Peppas (8). These results are dramatically altered if we now include the effect of hydrogen bonding, using equation 10. The effect of variations in χ is now greatly reduced, as can be seen from Figure 6, and the calculated values of \bar{M}_c are now much smaller. This is a consequence of the large contribution of hydrogen bonding to the chemical potential of the solvent, i.e., the $(\Delta G_H)_A$ term dominates the χ term. A calculated molecular weight of about 500, or "degree of polymerization" of about 2 clusters, between cross-link points is determined. This appears to be too small to be reasonable, but we will defer a discussion of this point until after we consider some additional data.

Lucht and Peppas (9) have also studied the swelling of various coals in pyridine, including PSOC 207 and PSOC 402. These swelling measurements were conducted at three different temperatures, 35, 60 and 80°C, and the results of applying equation 10 to their data is shown in Figures 7 and 8. It can be seen that there are distinct differences in the calculated values of the molecular weight between cross-link points with much larger values being determined at high temperatures. Unlike Lucht and Peppas (8), we allowed χ to have its usual $1/T$ dependence, while the variation of the values of the equilibrium constants, and hence $(\Delta G_H)_A$, with temperature was determined through the usual van Hoff relationship (14). Accordingly, it is not the temperature dependence of the solvent chemical potential that is responsible for such large differences. Only small variations might be expected due to the errors inherent in the various assumptions that are made concerning the form of the temperature dependence of the parameters over this fairly limited range. An explanation is immediately apparent if we examine the calculated solution phase diagrams shown in Figures 3 and 4, however. PSOC 207 and 402 are predicted to have upper critical solution temperatures near 75 and 125°C, respectively, these values being subject to the significant errors involved in estimating χ (19). Clearly, if the swollen network is at a temperature above this transition, in the single phase region, the coal should swell to the limit imposed by the nature of the network. Below this transition, however, there is a two phase region that is predicted for the coal primary chains in pyridine. The precise position of this transition for the network would be affected by the elastic forces between cross-link points, but clearly at some critical temperature solvent would be expelled leading to the phenomenon of gel collapse. The plots shown in Figures 7 and 8 suggest that this is precisely what we are observing in coal. PSOC 207 shows a large change in swelling and hence calculated molecular weight on going from 35°C to 60°C, but a small difference on going from 60°C to 80°C. In contrast, the major change for PSOC 402 appears to occur between 60°C and 80°C. We believe that these discontinuities in behaviour are due to expulsion of solvent from the swollen coal network. Our association model predicts this trend remarkably well; an examination of the calculated solution phase behaviours, shown in Figures 4 and 5, indicates that PSOC 402 has a higher UCST than PSOC 207. The absolute values of the transition are off by approximately 40°C, but this is not bad considering the errors in calculating χ and the probability that we should include a chain extension term in accounting for the phase behaviour of the gel.

If we now consider the values of the molecular weight obtained at the highest swelling temperature to be the most accurate, the predicted molecular weight between cross links is now more reasonable, but still small in terms of the inherent limitations of the model. If we further assume that the molecular weight of an average "cluster" is of the order of 200, this model predicts that the number of such

clusters between cross links is of the order of three for these coals. We must therefore, question whether it is at all appropriate to apply Flory's theory to coal, even in the modified form expressed by equation 10. We will suggest an alternative in the following section.

SWELLING BY DISINTERSPERSION

Even if we discount the flaws perceived by various authors in the original Flory-Rehner theory, its application to coal, even using the modified Gaussian statistics proposed by Kovac (32) and accounting for the contribution of hydrogen bonding, must be considered highly suspect. The results suggest that the number of aromatic "clusters" between crosslinks is small and such chains are certainly stiff. Nevertheless, we believe that it is possible to construct a simple model that provides at least a rough estimate of the molecular weight between cross-link points, although we do not formulate it in those terms.

This model is based on the very important observations of Bastide et al. (33) that the radius of gyration of the chains of a swollen polystyrene gel were equal, within the limits of experimental error, to that of the free chains in the same solvent, and did not vary when the degree of swelling was altered. On this basis it was proposed (34) that swelling was associated with a topological reorganization of the network, where the cross link points essentially rearrange their positions with only minor perturbations to the chain dimensions, a process that these authors labeled disinterspersion. We assume that the stiff molecules in coal essentially unfold in this manner and that the degree of swelling is then limited by the geometry of the system. A more complete account of our arguments is given in reference 1, but a schematic view of this process is illustrated in Figure 9. Strangely enough, we will argue that the coal "chains" are not straight rods, as shown in this figure, but follow random walk or perhaps self avoiding walk statistics. This is a second crucial point in the development of our simple model. It is important to realize that we are not making this claim on the basis of any argument concerning chain flexibility. Instead, we propose that this is a consequence of the heterogeneity of linkages that must occur in coal. A two dimensional view of simple aromatic units (benzene and naphthalene rings), linked by $-CH_2-$ and $-O-$ groups, is shown in Figure 10. Even if we require on steric grounds that bonds in the ortho position are unlikely, the variety of other possibilities result in a chain that can be modeled by a set of virtual bonds, in this example shown linking the centers of the aromatic clusters, such that they trace out a (more-or-less) random walk or random flight. If the network then simply swells to the limit permitted by the "unfolding" of these chains, which behave as stiff, bent wires, then the relationship between the degree of swelling and the contour length of these chains follows from simple geometry. If we let the functionality of the network be equal to f and the average end-to-end distance between cross link points be equal to $R_0 (= \langle r^2 \rangle^{1/2})$, then we can pick a cross-link point in the swollen network at random and determine the volume of the chains in the volume $(4/3) \pi R_0^3$ following Bastide et al. (34). This is equal to $fV_s N$, where V_s is the volume occupied by each "repeat" unit and N is the number of repeat units in each primary chain. It then follows that the volume fraction of polymer in the swollen gel is given by

$$\phi = \frac{3fV_s N}{4N\pi R_0^3} \quad (11)$$

The quantity R_0 is related to N by the general relationship

$$R_0 = aN^v \quad (12)$$

where a is the length of an average unit and v has a value in the range 0.5 to 1 (for a random walk $v = 0.5$, a self avoiding walk $v = 0.6$ and for a rigid rod $v = 1$).

The parameter a , V_s and N are not easily defined for any particular coal, but, as we show in more detail in a separate publication (21), by defining these quantities on a per carbon atom basis we obtain

$$N_c^{(3v-1)} = \frac{3fV_c}{4\pi\phi a_c^3} n_c^{3(v-1)} \quad (13)$$

where N_c is the number of carbon atoms between cross-link points, V_c is the molar volume per carbon atom (which can be determined from the elemental composition and density), and a_c is the length of such a cluster (or virtual bond in Figure 10) divided by the number of carbon atoms (n_c , in that cluster. If we assume that as a result of the heterogeneities of the cross-link points and the limited degree of chain flexibility that can occur in a good solvent, $v = 0.6$, then plots of N_c vs n_c for various values of a_c can be constructed, as shown in Figure 11 (a value of $f = 3$ was assumed). The data used to obtain these plots was that of the Illinois #6 coal studied by Larsen et al. (7). If we assume an average of 8-9 carbon atoms per repeat or cluster, corresponding to a mixture of substituted benzene and naphthalene rings, with the former predominating, then it follows from known bond length and bond angle geometries that a_c is in the range 0.5 to 0.6, so that N_c would have a value somewhere between 25 and 45 carbon atoms, corresponding to approximately 3-5 clusters between each cross-link point. For a network with $f = 4$, this increases to a value between 4 and 7 (19).

CONCLUSIONS

We believe a number of important conclusions follow from this analysis, amongst the most significant of which are:

- 1) Solubility parameters for coal are not accurately determined from swelling measurements because of free volume effects.
- 2) The phase behaviour of the coal network/solvent has to be taken into account when conducting swelling measurements.
- 3) We predict that the phenomenon of gel collapse could occur in coal.
- 4) A simple model for coal swelling based on disinterspersation has been proposed, following the work of Bastide et al. (33,34).

ACKNOWLEDGEMENTS

We gratefully acknowledge the support of the Office of Basic Energy Sciences, Division of Chemical Sciences, Department of Energy, under Grant No. DE-FG02-86ER13537.

REFERENCES

1. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca: NY, 1953.
2. Flory, P. J. *Selected Works of Paul J. Flory*; Mandelkern, L., Mark, J. E., Suter, U. W., Yoon, Do. Y., Eds.; Stanford University Press: Stanford, CA, 1985; Vol. I-III.
3. van Krevelen, D. W. *Coal*; Elsevier: New York, 1981.
4. van Krevelen, D. W. *Fuel* 1966, 45, 229.
5. Green, T.; Kovac, J.; Brenner, D.; Larsen, J. W. In *Coal Structure*; Meyers, R. A., Ed.; Academic: New York, 1982.
6. Larsen, J. W. In *Chemistry and Physics of Coal Utilization*; AIP Conference Proceedings, 70; Cooper, B. R., Petrakis, L., Eds.; AIP: New York, 1981.
7. Larsen, J. W.; Green, T. K.; Kovac, J. J. *Org. Chem.* 1985, 50, 4729.
8. Lucht, L. M.; Peppas, N. A. In *Chemistry and Physics of Coal Utilization*, AIP Conference Proceedings 18; Cooper, B. R., Petrakis, L., Eds.; AIP: New York, 1981.
9. Lucht, L. M.; Peppas, N. A. *Fuel* 1987, 66, 803.
10. Lucht, L. M.; Peppas, N. A. *J. Appl. Polym. Sci.* 1987, 33, 2777.
11. Brenner, D. *Fuel* 1985, 64, 167.

12. DeGennes, P. G., Scaling concepts in Polymer Physics, Cornell University Press, Ithaca, NY, (1979).
13. Painter, P. C.; Park, Y.; Coleman, M. M., Macromolecules, 1988, 21, 66.
14. Painter, P. C.; Park, Y.; Coleman, M. M., Macromolecules, 1989, 22, 570.
15. Painter, P. C.; Park, Y.; Coleman, M. M., Macromolecules, 1989, 22, 580.
16. Painter, P. C., Graf, J. and Coleman, M. M. J. Chem. Phys. (submitted for publication).
17. Painter, P. C., Park, Y. and Coleman, M. M., Energy and Fuels, 1988, 2, 693.
18. Painter, P. C., Park, Y., Sobkowiak, M. and Coleman, M. M., ACS Fuel Chem. Div. Preprints, 1989, 34(2), 559.
19. Painter, P. C., Graf, J. and Coleman M. M., (to be submitted to Energy and Fuels).
20. Painter, P. C., Park, Y., Sobkowiak, M. and Coleman, M. M. (to be submitted to Energy and Fuels).
21. Painter, P. C., Graf, J., and Coleman, M. M. (to be submitted to Energy and Fuels).
22. van Krevelen, D. W. Fuel 1966, 45, 229.
23. van Krevelen, P. W., Properties of Polymers; Elsevier: Amsterdam, 1972.
24. Hoy, K. L., J. Paint Technol., 1970, 42, 76.
25. Small, P. A., J. Appl. Chem., 1953, 3, 71.
26. Bristow, G. M. and Watson W. F., Trans. Faraday, Soc., 1958, 54, 1731.
27. Biro, J. Zeman, L. and Patterson, D. Macromolecules, 1971, 4, 30.
28. Sanchez, I. C. and Lacombe, R. H. J. Phys. Chem. 1976, 80, 2352, 2568.
29. Sanchez, I. C. and Lacombe, R. H. Macromolecules, 1978, 11, 1145.
30. Sanchez, I. C. and Lacombe, R. H. J. Pol. Sci. Poly Letters Ed, 1977, 15, 71.
31. Painter, P. C., Graf, J. and Coleman, M. M., to be published.
32. Kovac, J. Macromolecules, 1978, 11, 362.
33. Bastide, J., et al., as reported by Candau, S., Bastide, J. and Delsanti, M., Advances in Polymer Science, 1982, 44, 27.
34. Bastide, J., Picot, C., Candau, S., J. Macromol. Sci., Phys. 1981, B19, 13.

Table 2. Parameters for Solvents at 25°C

SOLVENTS	V_s ($\text{cm}^3 \text{ mol}^{-1}$)	K_A (kcal mol^{-1})	h_s (kcal mol^{-1})	δ_s (cal cm^{-3}) ^{1/2}
PYRIDINE	81	284.87	8.9	10.6
THF	74.3	89.54	5.76	9.9
ACETON	74.3	58.9	4.03	9.9
DIETHYL ETHER	101.7	45.24	5.76	7.5
ACETONITRILE	55.4	23.56	2.03	11.8
BENZENE	82.2	1.41*	1.25	9.1

* Weak H-bonds between OH groups and π electrons have been proposed.

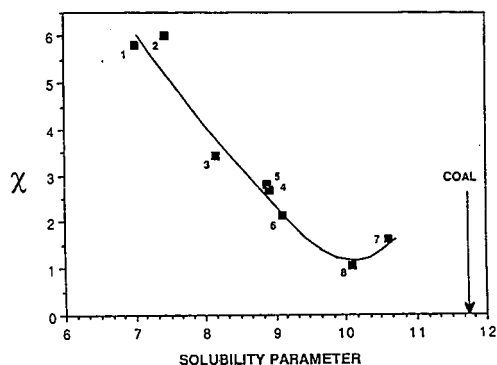


Figure 1. Plot of χ vs solubility parameters for the Illinois #6 coal and solvents studied by Larsen et al. (7).

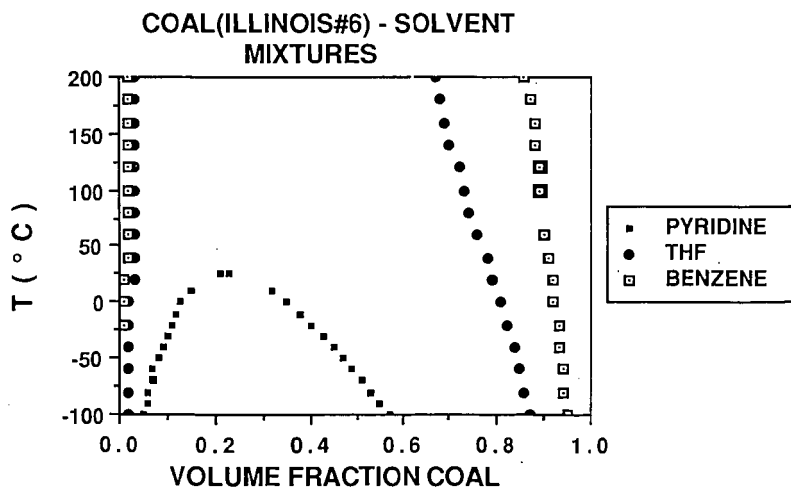


Figure 2. Phase diagram (spinodals) for an Illinois #6 coal mixed with various solvents.

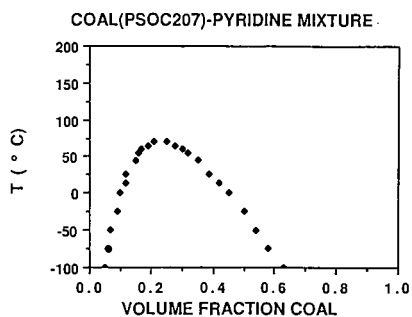


Figure 3. Phase diagram (spinodal) for PSOC 207-pyridine mixtures.

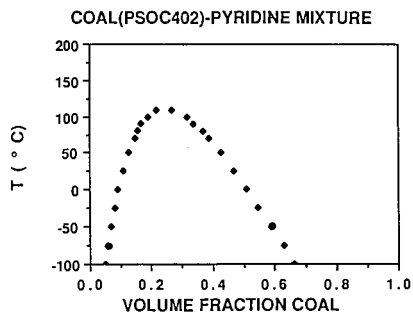


Figure 4. Spinodal for PSOC 402/pyridine mixtures.

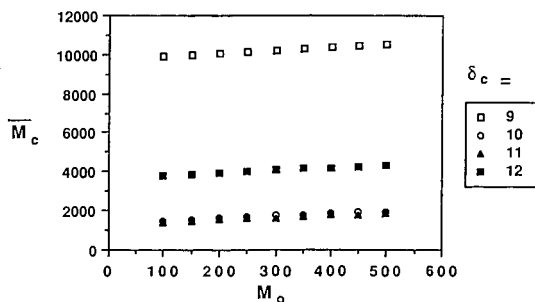


Figure 5. Plot of \bar{M}_c vs M_o (see text) for Illinois #6 coal, ignoring hydrogen bonds.

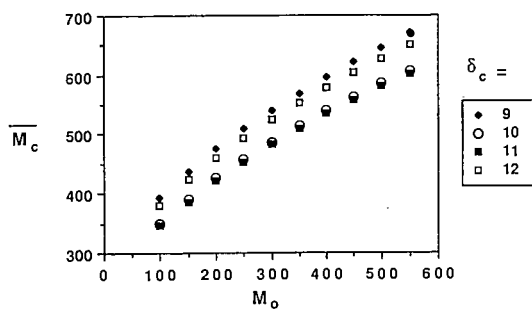


Figure 6. Plot of M_c vs M_o for Illinois #6 coal when hydrogen bonding is included.

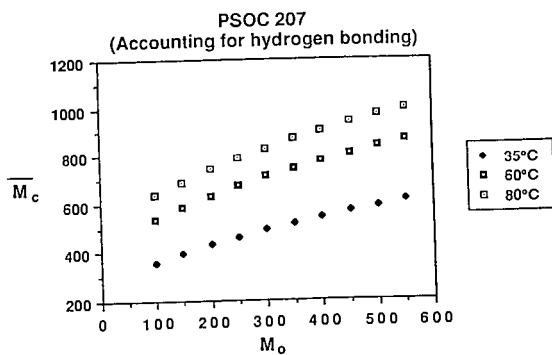


Figure 7. M_c vs M_o for PSOC 207.

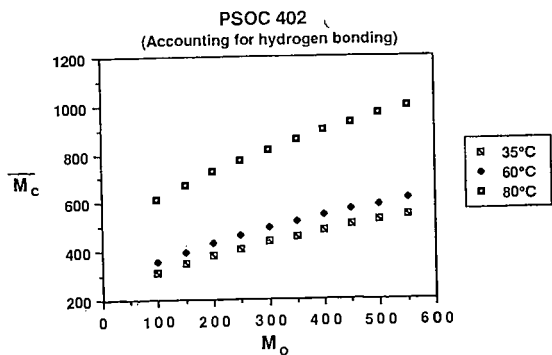


Figure 8. M_c vs M_o for PSOC 402

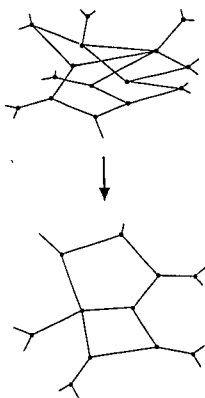


Figure 9. Disinterspersion for a network of rigid rods.

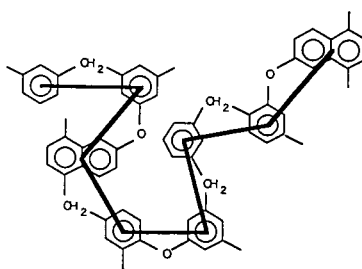


Figure 10. A random walk imposed by a pattern of substitution in a rigid chain.

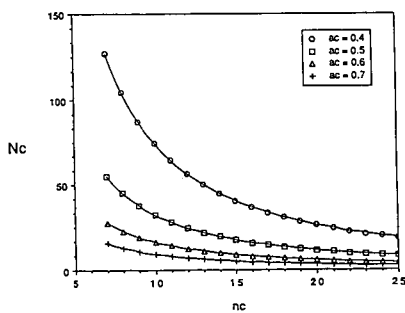


Figure 11. Plot of N_c (number of carbon atoms between cross link points) vs n_c (the number of carbon atoms per cluster).